



COLLÈGE
DE FRANCE
— 1530 —

*Chaire de Physique
de la Matière Condensée
Antoine Georges*

Contrôle des fonctionnalités des oxydes

Hétéro-structures, Impulsions Lumineuses

Cours 3

*1) Introduction à la structure électronique des
oxydes (suite du cours 2)*

2) Introduction aux Nickelates $RNiO_3$

Cycle 2016-2017
9 mai 2017



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Control of oxide functionalities: Heterostructures, Light pulses

Lecture 3

- 1) *Introduction to the electronic structure of oxides*
(cont'd from lecture 2)
- 2) *Introduction to Nickelates $RNiO_3$*

Slides will be in English

2016-2017 Lectures
May 9, 2017

Today's seminar – May 9

Marcelo Rozenberg

LPS-Orsay

(currently visiting UC-San Diego)

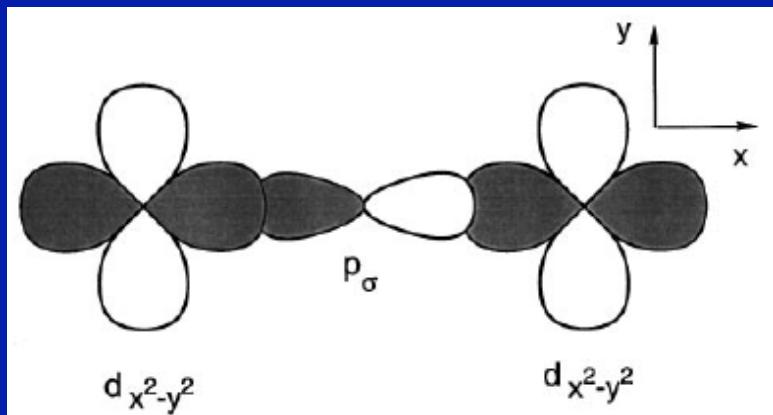
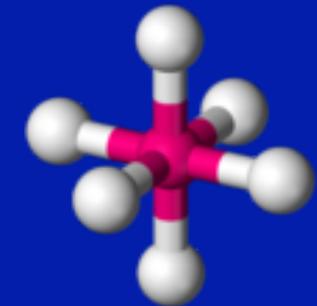
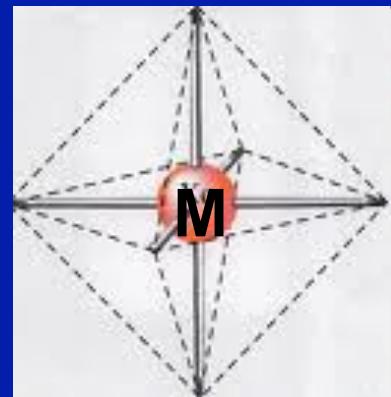
Transition-metal oxides under strong electric fields, from resistive switching to artificial synapses and neurons



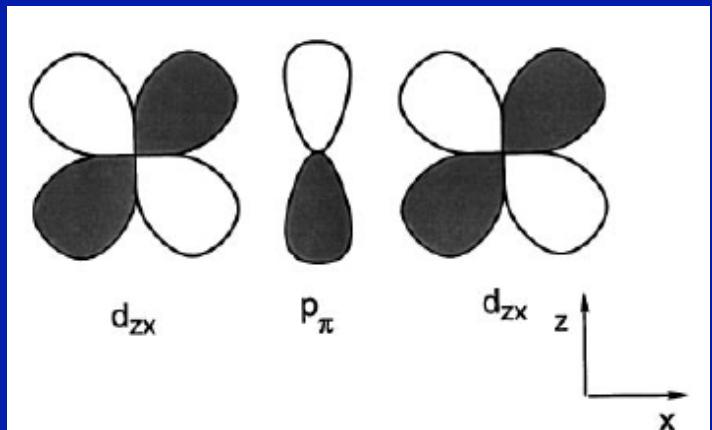
Lecture 2 (overview/summary)

- Crystal structure of oxides: perovskites ABO_3 [RMO_3]
- The Ruddlesden-Popper series $\text{R}_{n+1}\text{M}_n\text{O}_{3n+1}$
- Metallic behavior out of 2 insulators in the heterostructure LTO/STO
- Distortion of perovskites: tilts and rotations.
Tolerance factor and Glazer notations.
- Crystal-field theory: lifting orbital degeneracy of the d-shell from the ligand environment.

Crystal-field splitting in octahedral environment :



e_g orbitals point towards oxygen atoms(sigma-bonding)
→ feel larger Coulomb potential
→ pushed to higher energy



t_{2g} orbitals point away from oxygen atoms(pi-bonding)
→ feel smaller Coulomb potential
→ lower energy than e_g

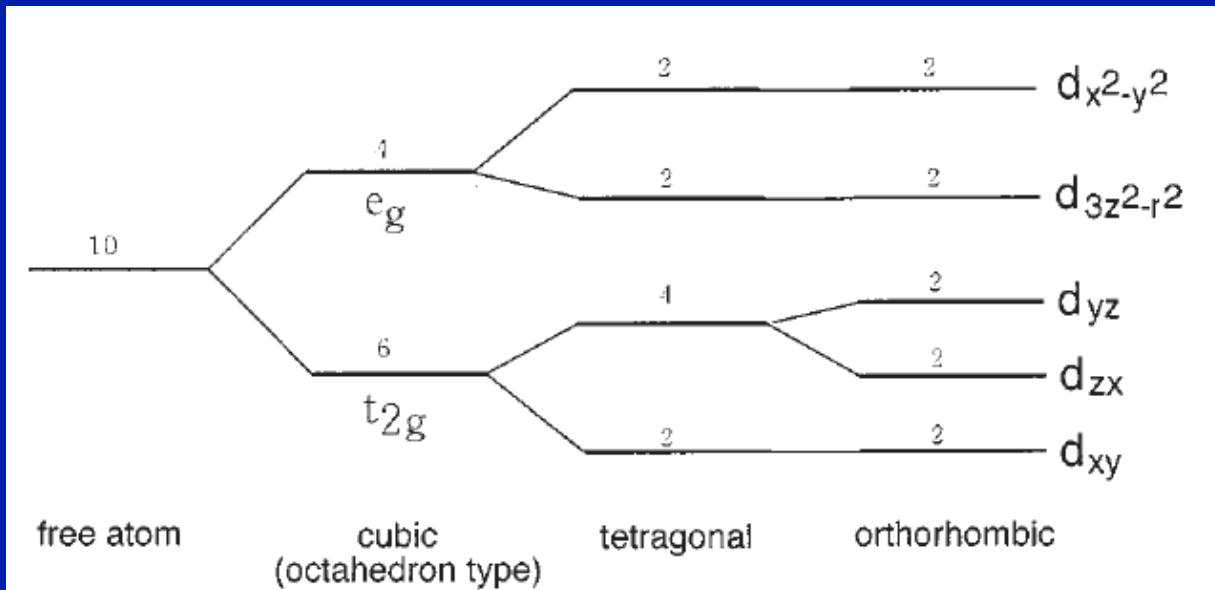


FIG. 2. Crystal-field splitting of 3d orbitals under cubic, tetragonal, and orthorhombic symmetries. The numbers cited near the levels are the degeneracy including spins.

Intra e_g splitting

Intra- t_{2g} splitting

Lowering further the crystal symmetry (distort from cubic)
Induces additional lifting of degeneracy

Orthohrombic perovskite → Fully lifted

Tetrahedral environment (MO_4): e_g has lower energy, t_{2g} higher

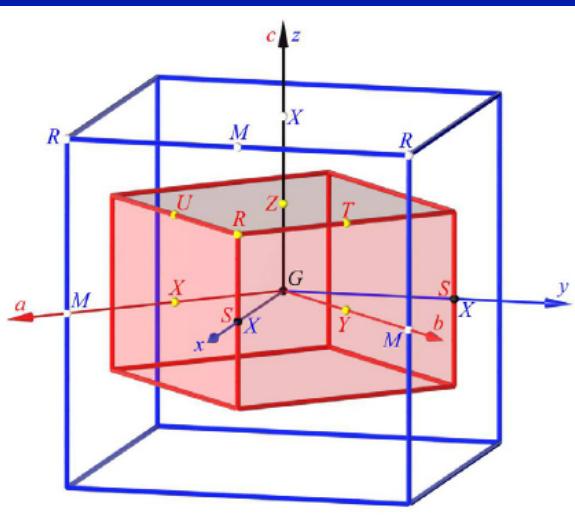
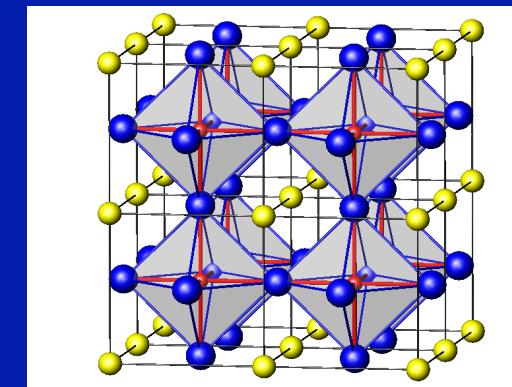
1. From Crystal-Field Theory to Band Structure

From the atom to the full solid: energy bands of oxides

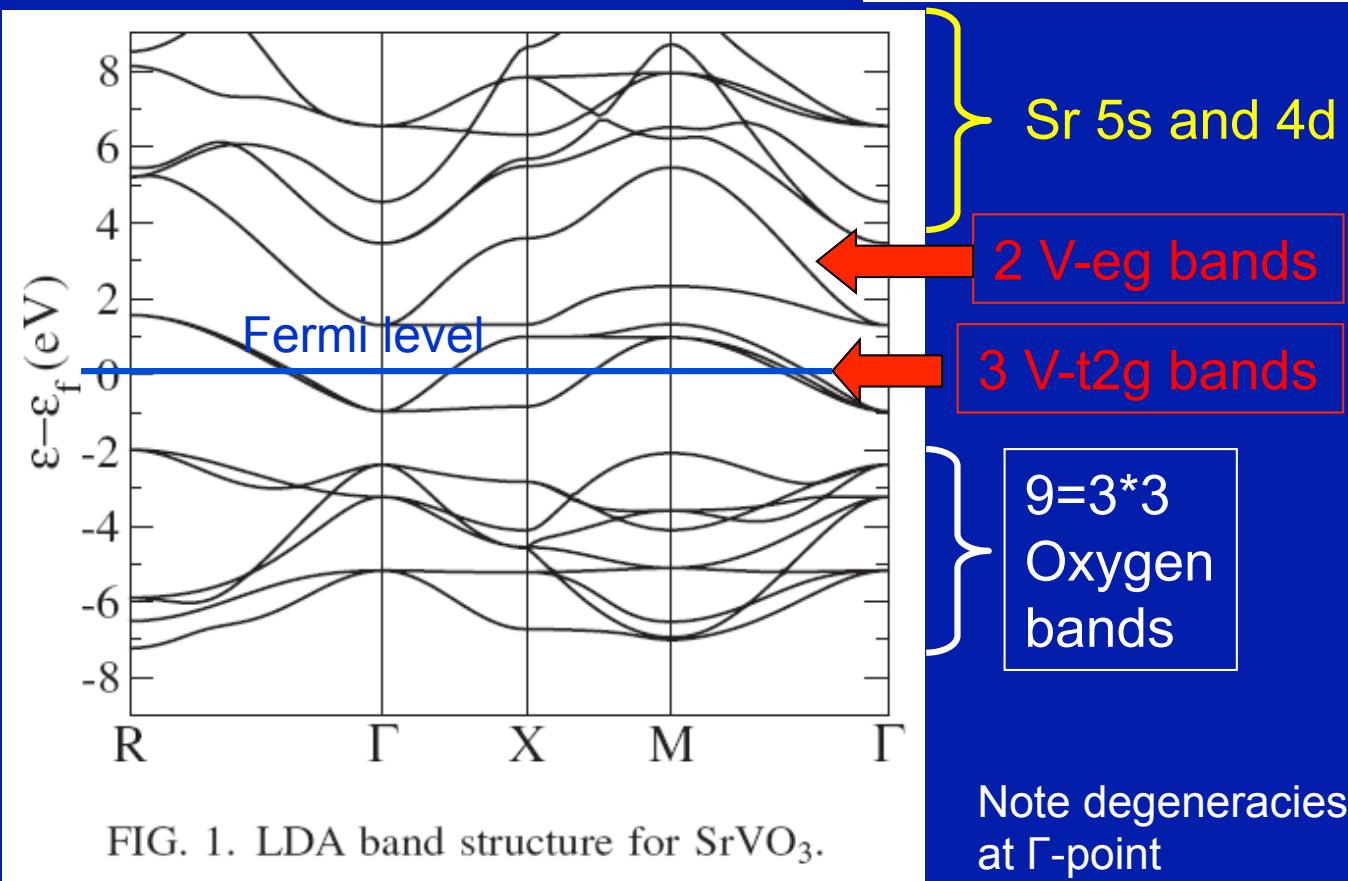
(or: how to make sense of a plate of spaghetti...)

A simple case: cubic SrVO_3

Band structure from DFT-LDA:

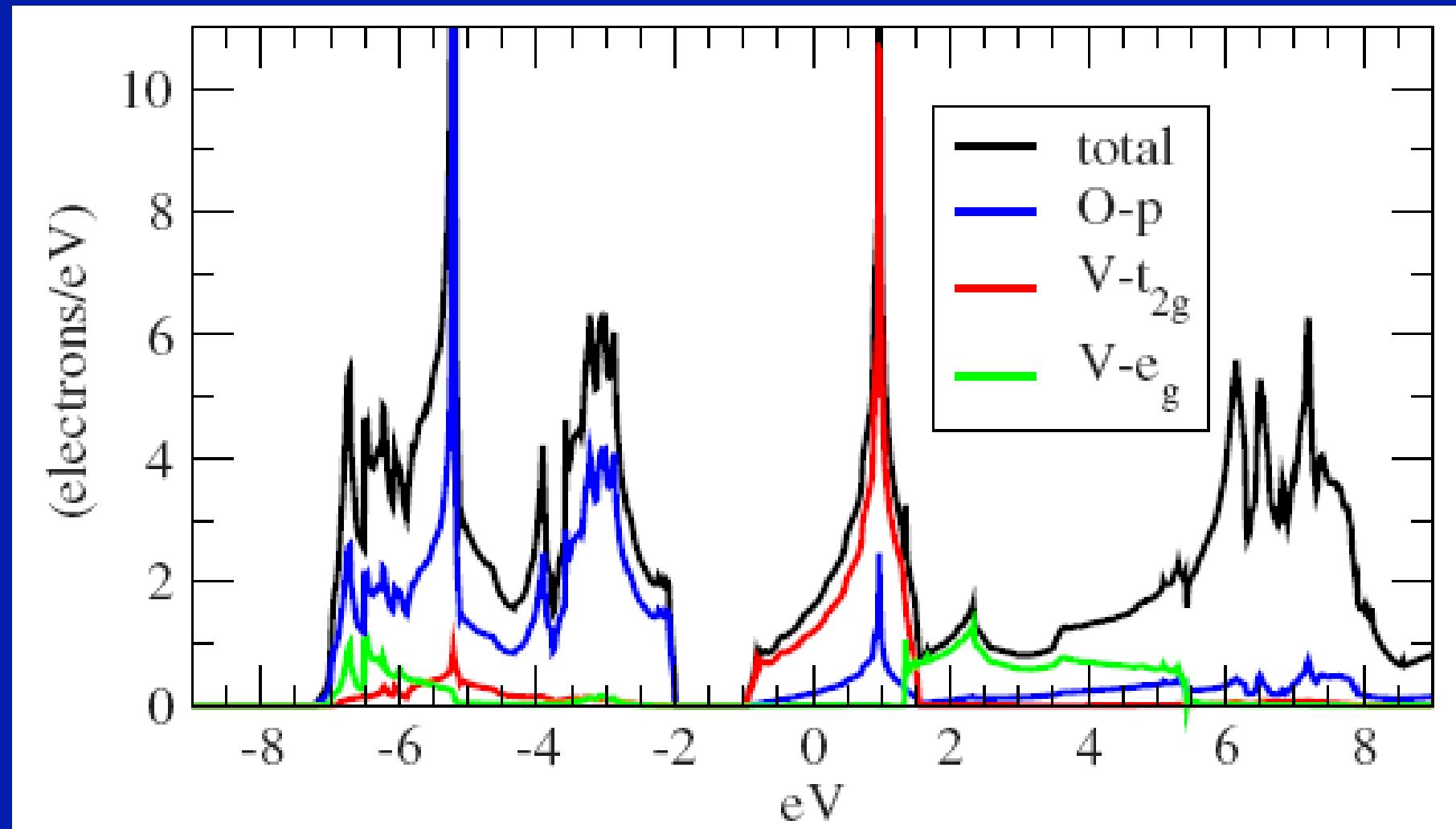


Pavarini et al.
PRL 92 (2004) 176403
New J.Phys 7 (2005) 188
Amadon et al.
PRB 77 (2008) 205112



Density of states:

(orbitally-resolved, i.e projected on ~ atomic orbitals)



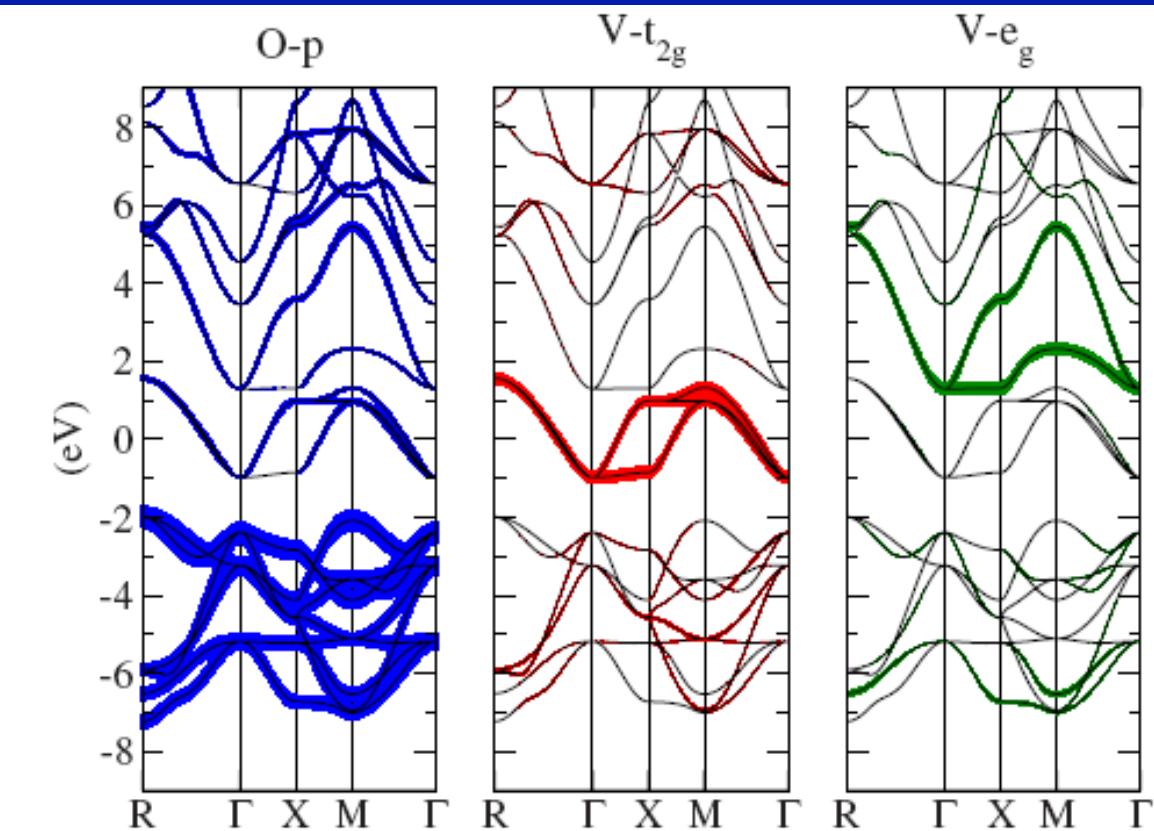
Strong mixing of V-eg states with oxygen

t_{2g} bandwidth ~ 2.6 eV

To understand orbital character better, plot 'fat bands:

Project Bloch functions onto atomic-like orbitals and
plot matrix element at each k-point:

$$|\langle \psi_{\mathbf{k}\nu} | \phi_{lm} \rangle|^2$$



Mixing of oxygen
with d-states obvious,
especially for eg

FIG. 3. (Color online) LDA band structure for SrVO₃ computed in PAW, with “fatbands” to show the amplitude of the projection of each band on a given atomic orbital (O *p*, V *t*_{2g}, and V *e*_g).

Summarize key infos from band-structure, in this (quite) simple case:

- t_{2g} manifold of 3 bands well-separated from oxygen (below) and e_g bands (above)
- t_{2g} bands occupied by 1 electron in total (as requested)
- t_{2g} bandwidth around 2.6 eV
- Distance between center of t_{2g} and center of oxygen band: about 6.5 eV (only 1eV from top of O to bottom of t_{2g} though) → ‘charge-transfer energy’ is large
- Bandstructure (LDA) is that of a METAL
- Effective mass (from specific heat) is found to be roughly a factor of 2 larger than the one from LDA, or equivalently: measured Fermi velocity is about 2 times smaller → Effect of electronic correlations

More on the bandwidth: hopping is via oxygen

- Each Vanadium is in a cage of 6 oxygens

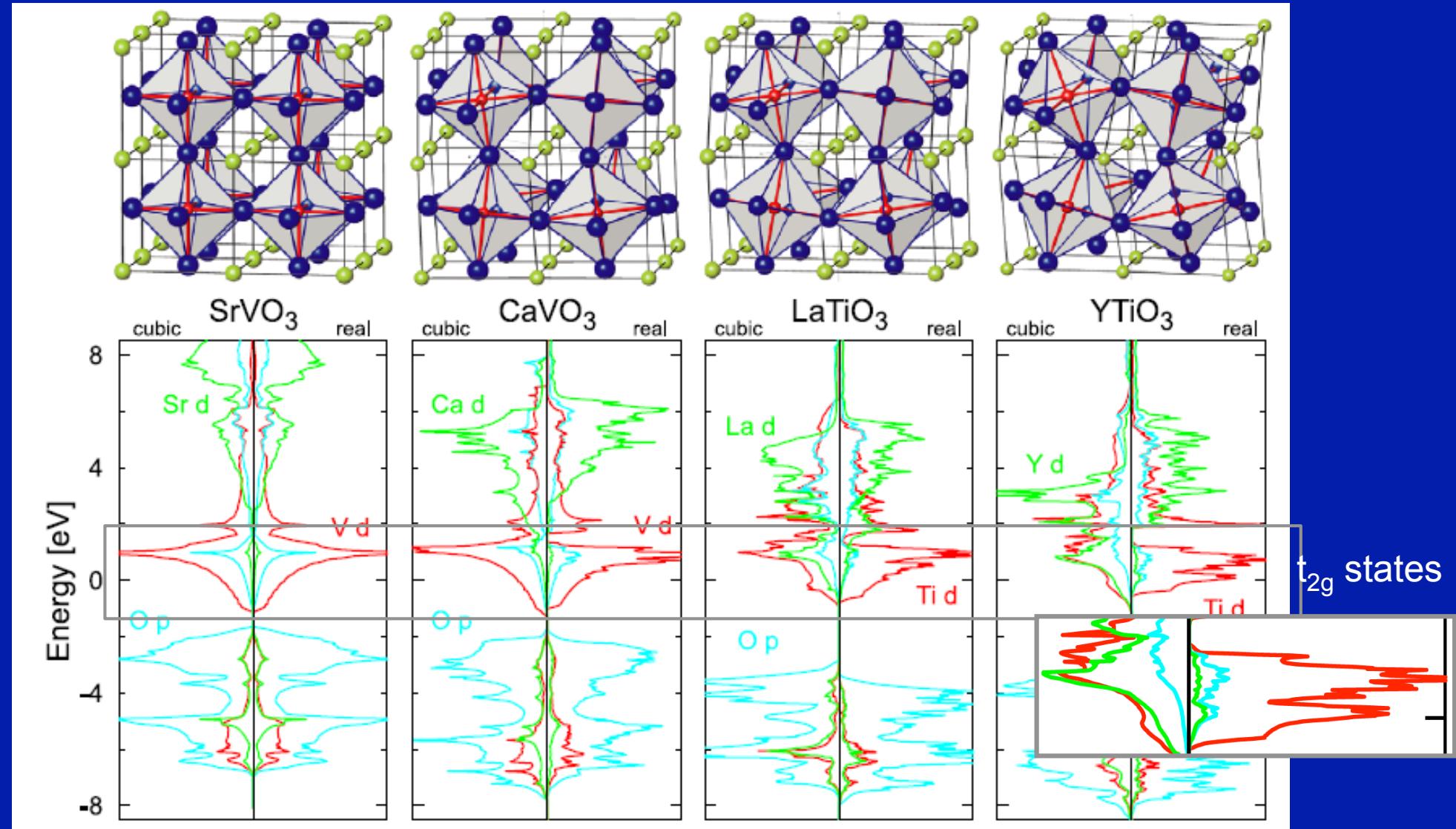
→ Direct d-d hopping is difficult, hence direct t_{dd} is small
(this is one of the two main differences between a pure Transition metal and its oxide, the other one being that the 4s orbital is empty in the oxyde → oxydes have narrow bands)

- Hopping of electrons on V-sites occurs through hybridization between O p-orbitals and V d-orbitals, with amplitude t_{pd}

- Roughly, when the charge-transfer energy Δ (see below) is large, the amplitude of the effective d-d hopping is of order:

$$t_{\text{eff}}^{dd} \sim t_{pd}^2 / \Delta$$

Effects of the orthorhombic [$a^-a^-c^+$] distortion: SrVO_3 , CaVO_3 , LaTiO_3 , YTiO_3 (all d¹, ALL METALS in DFT-LDA !)



Left panels: hypothetical cubic; Right panel: real structure

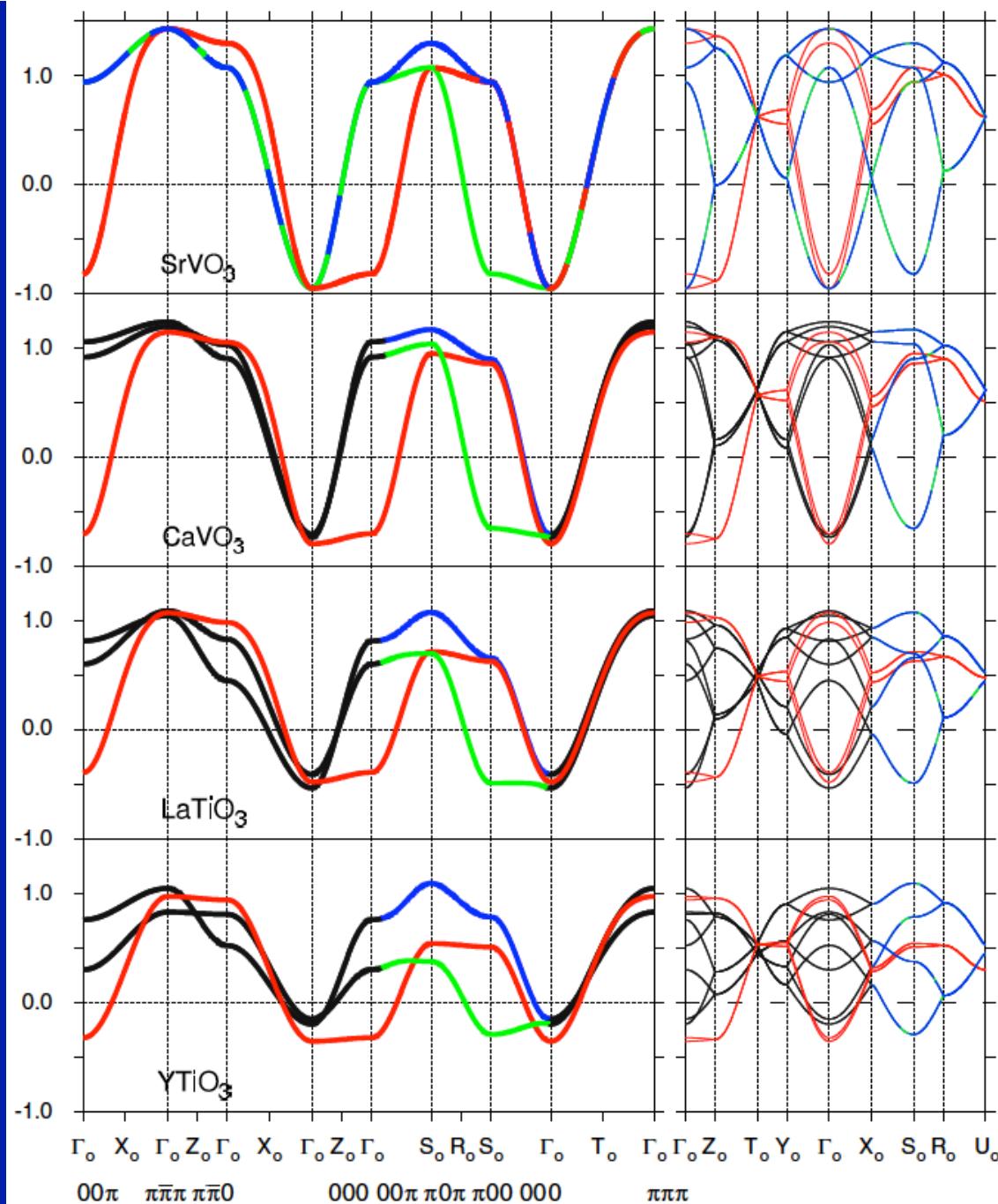


Figure 11. Cubically averaged ($\mathbf{Q} = \mathbf{0}$) t_{2g} LDA bandstructures in eV, in the primitive monoclinic BZ (left), and folded into the orthorhombic BZ (right).

The two effects of distortion:

- 1) Reduction of total t_{2g} bandwidth:

Table 8. t_{2g} edge-to-edge ($W_{t_{2g}}$) and rms (W) bandwidths in eV.

	SrVO ₃ [42]	CaVO ₃ [43]	LaTiO ₃ [44]	LaTiO ₃ [12]	YTiO ₃ [20]
$W_{t_{2g}}$	2.85	2.45	2.09	1.92	2.05
W	2.85	2.39	2.18	2.08	1.87

This is because the O-M-O bond is no longer straight
→ pi-bonding less efficient

- 2) Splitting between t_{2g} orbitals (lifting of orbital degeneracy)

(140,200) meV for LaTiO₃ ;
(200,330) meV for YTiO₃



→ **Both effects** are responsible for the Mott insulating nature of LaTiO₃ and YTiO₃ (as we shall see below)

Tilts/rotations in a t_{2g} system: covalency between O and A-site cation (Sr,La) !

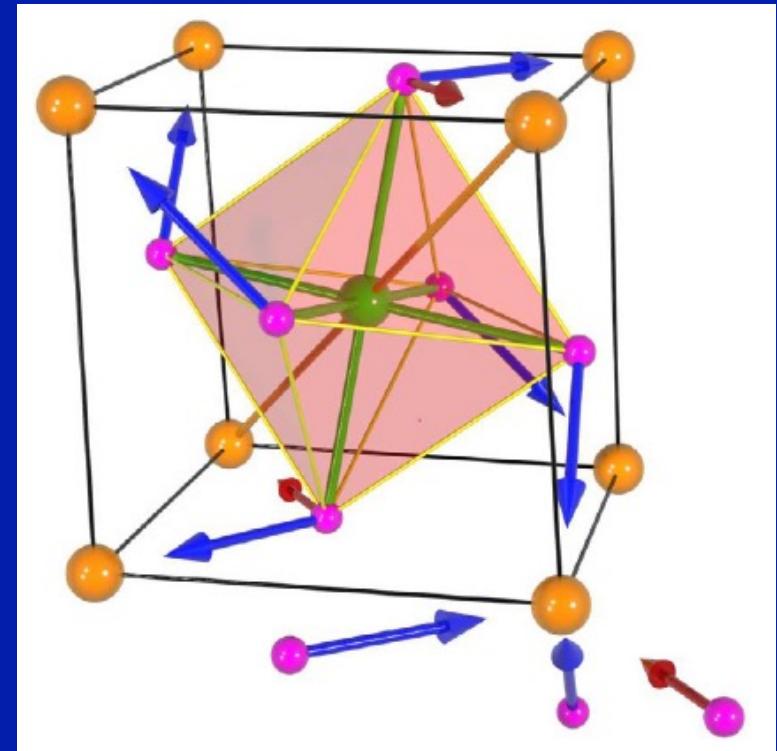


Figure 7. Schematic representation of the O-A covalent bonds shown for LaTiO₃ in figures 5 and 6: O1 binds to *two* while O2 binds to *one* of the four A-neighbours. One of the two O1-A bonds is relatively weak and is indicated by a short, red arrow. The resulting GdFeO₃-type distortion shortens the O-A bonds correspondingly. In CaVO₃, LaTiO₃, and YTiO₃, the shortest O1-A bond is shortened by respectively 10, 17, and 28% with respect to the average, the 2nd-shortest O1-A bond by respectively 4, 11, and 23%, and the shortest O2-A bond by respectively 12, 16, and 22%. The oxygen coordination of the A-ion is reduced from 12 to 4, with two of the near oxygens being in the horizontal, flat face of the distorted A-cube, and the two others in *one* of the vertical, buckled faces. The A-B-A diagonal (orange bar) lying in the plane of the short, red arrows is shortened by respectively 3, 7, and 9% of the average. The unit shown is the front bottom left one (subcell 1) seen in e.g. figure 2.

Why are 113 Vanadates metallic and 113 Titanates insulating ?

- 1 electron in the 3d shell
- Very similar values of the Hubbard U
- Similar electronic structure ...

- SrVO_3 [V⁴⁺, d¹]: A metal with signatures of sizeable but moderate e-e correlations ($m^*/m \sim 2.5$)
- CaVO_3 [V⁴⁺, d¹]: A metal with stronger electronic correlations ($m^*/m \sim 3.5$)
- LaTiO_3 [Ti³⁺, d¹]: A small-gap insulator (~ 0.2 eV)
- YTiO_3 [Ti³⁺, d¹]: A larger gap insulator (~ 1 eV)

When do we have a metal and
when a Mott insulator ?

*A simple-minded, qualitative,
criterion*

Assume that only the d-shell plays a role
during electron transfer

(i.e all relevant electronic configurations have a
fully filled O²⁻ Ligand shell)

Ground-state has configuration dⁿ

Hopping one electron from one site to the next:

$$d^n \ d^n \rightarrow d^{n+1} \ d^{n-1}$$

Energy cost of this process:

$$\begin{aligned} U_{\text{eff}} &= E_0(n+1) + E_0(n-1) - 2E_0(n) \\ &= [E_0(n+1) - E_0(n)] - [E_0(n) - E_0(n-1)] \equiv I - A \end{aligned}$$

Typical kinetic energy gained in the process: E_K (~ bandwidth W)

$U_{\text{eff}} \gtrsim E_K \Rightarrow$ (Mott)Insulator

$U_{\text{eff}} \lesssim E_K \Rightarrow$ Metal

What is U_{eff} ?

- This is a fairly subtle question, which depends on:
- How we choose to describe the system (i.e. which bands/orbitals we retain)
- Screening, in accordance with this choice
- The specific electronic configuration of each shell taking part in the electron transfer process, in accordance with Hund's rules.

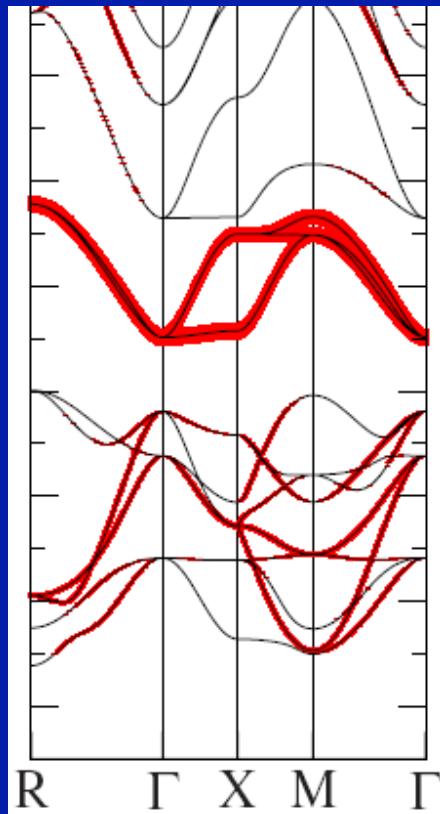
*A whole set of lectures could be devoted to this issue
(and certainly entire workshops/conferences are...)*

Effective model depends on choice of selected energy range

Decide for which bands (or rather: for which energy window) an effective model will be constructed

V- t_{2g} states only
(3 bands)

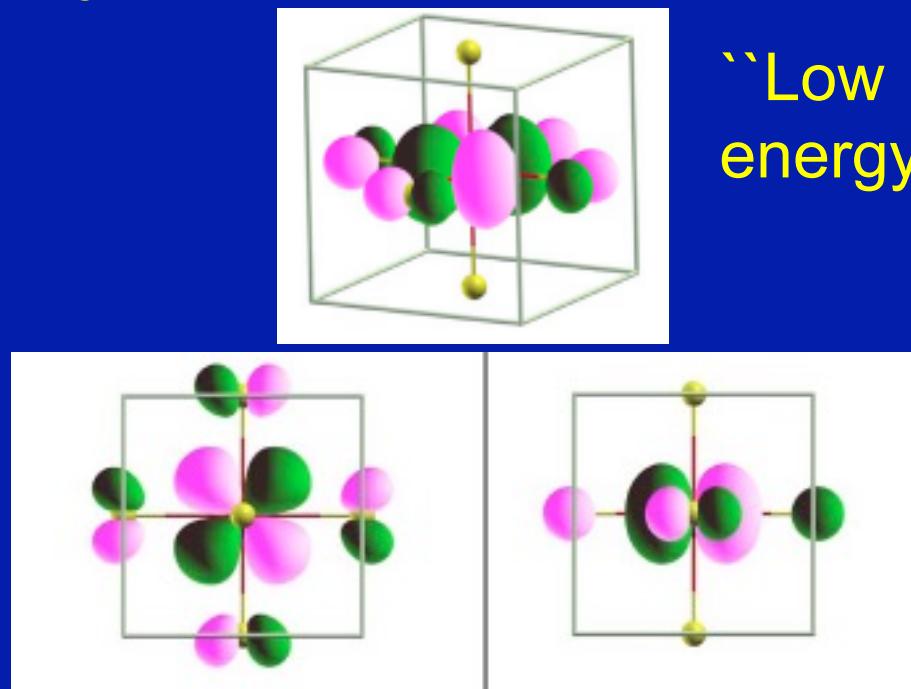
Small energy window
→Wannier functions
will leak on oxygen
sites to capture
V-O hybridization



V- t_{2g} and e_g states
And O –states
(14 bands)

Large energy window
→Wannier functions
are quite localized
and atomic-like

t_{2g} only: extended Wanniers



“Low
energy”

$V\ t_{2g}+e_g$ and O:
very localized Wanniers

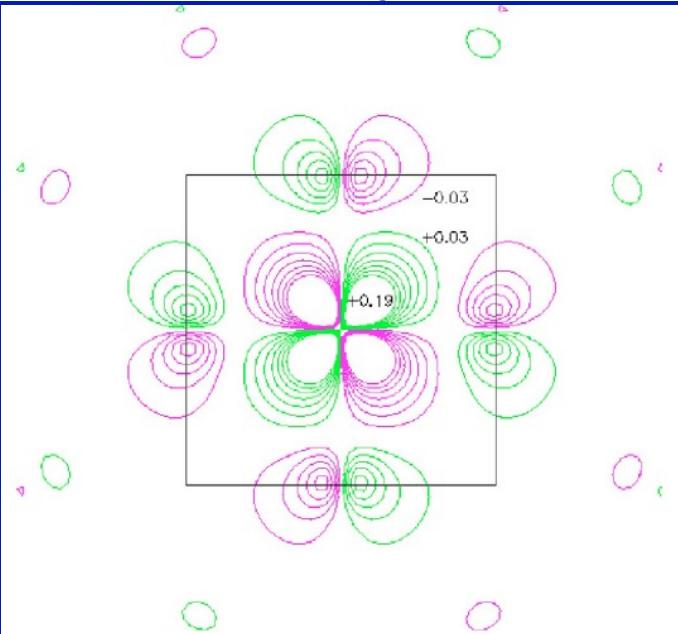
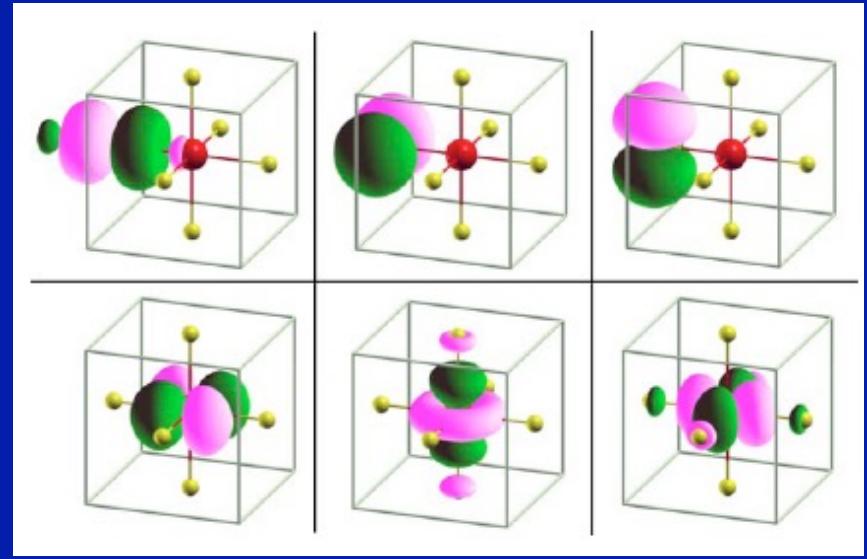


FIG. 7. (Color online) Distinct WFs for SrVO_3 obtained from the MLWF construction using the MBPP code. First row: $O(p_x)$, $O(p_y)$, and $O(p_z)$ for a chosen oxygen site. Second row: $V(t_{2g}, xy)$ as well as $V(e_g, 3z^2 - r^2)$ and $V(e_g, x^2 - y^2)$. The contour value for each of the MLWFs was chosen as $0.05 \text{ (a.u.)}^{-3/2}$.

F.Lechermann et al.
Phys Rev B 74 (2006) 125120

Corresponding models (very schematic – ignoring important ‘details’)

Full d-p:

$$\begin{aligned} & -t_{pd} \sum_{i \in M} \sum_{j \in O} d_i^\dagger p_j + \varepsilon_d \sum_i d_i^\dagger d_i + \varepsilon_p \sum_j p_j^\dagger p_j + \\ & + \frac{1}{2} U_{dd} \sum_i \hat{n}_{di} (\hat{n}_{di} - 1) + \text{other interactions...} \end{aligned}$$

Low-energy (extended Wanniers on M-sites):

$$-\tilde{t} \sum_{ii' \in M} c_i^\dagger c_{i'} + \frac{1}{2} \tilde{U} \sum_{i \in M} \hat{n}_i (\hat{n}_i - 1) + \dots$$

\tilde{t} : Effective hopping associated with Wannier functions for metal bands

\tilde{U} : Effective interaction, including screening from states not retained in the low-energy effective hamiltonian

More about interactions

For simplicity, I will not describe here the full structure of interactions for a 5-orbital d-shell
(i.e. Slater-Racah parametrization of $U_{m_1 m_2 m_3 m_4}$)
→ see my 2009-2010 College de France lectures

I will instead focus on ‘low-energy’ descriptions involving a t_{2g} (3-fold) or e_g (2-fold) shell in cubic symmetry
(→ Kanamori hamiltonian)

For a t_{2g} triplet, only 3 independent Coulomb integrals:

$$\begin{aligned} U &= \int d\mathbf{r} d\mathbf{r}' |\phi_m(\mathbf{r})|^2 V_c(\mathbf{r}, \mathbf{r}') |\phi_m(\mathbf{r}')|^2 \\ U' &= \int d\mathbf{r} d\mathbf{r}' |\phi_m(\mathbf{r})|^2 V_c(\mathbf{r}, \mathbf{r}') |\phi_{m'}(\mathbf{r}')|^2 \quad m \neq m' \\ J &= \int d\mathbf{r} d\mathbf{r}' \phi_m(\mathbf{r}) \phi_{m'}(\mathbf{r}) V_c(\mathbf{r}, \mathbf{r}') \phi_m(\mathbf{r}') \phi_{m'}(\mathbf{r}') \end{aligned}$$

Indeed:

$J=J'$ (real wave-functions)

$U_{m'mmm}=0$ by symmetry

V_c : SCREENED Coulomb interaction in the solid

Hence, Kanamori hamiltonian:

[J.Kanamori, Prog. Theor. Phys. 30 (1963) 275]

$$\begin{aligned} H_K = & U \sum_m \hat{n}_{m\uparrow} \hat{n}_{m\downarrow} + U' \sum_{m \neq m'} \hat{n}_{m\uparrow} \hat{n}_{m'\downarrow} + (U' - J) \sum_{m < m', \sigma} \hat{n}_{m\sigma} \hat{n}_{m'\sigma} + \\ & - J \sum_{m \neq m'} d_{m\uparrow}^+ d_{m\downarrow} d_{m'\downarrow}^+ d_{m'\uparrow} + J \sum_{m \neq m'} d_{m\uparrow}^+ d_{m\downarrow}^+ d_{m'\downarrow} d_{m'\uparrow} \end{aligned}$$

EXACT for a t_{2g} shell (also e_g)

Useful reference: Sugano, Tanabe & Kamimura,
Multiplets of transition-metal ions in crystals
Academic Press, 1970

Furthermore, spherical symmetry of the screened interaction V_c would imply that:

$$U' = U - 2J$$

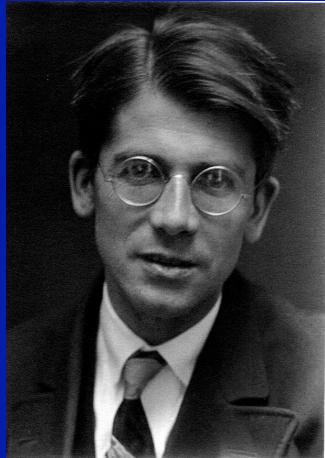
In the solid, this can only be approximate, but is usually still a good approximation (however, needs to keep in mind that this may not be true in all materials)

Under this assumption, the hamiltonian can be written (Kanamori):

$$H_{t_{2g}} = (U - 3J) \frac{\hat{N}(\hat{N} - 1)}{2} - 2J \vec{S}^2 - \frac{J}{2} \vec{L}^2 + \frac{5}{2} J \hat{N}$$

With the total charge, spin and orbital iso-spin generators:

$$\hat{N} = \sum_{m\sigma} \hat{n}_{m\sigma}, \quad \vec{S} = \frac{1}{2} \sum_m \sum_{\sigma\sigma'} d_{m\sigma}^\dagger \vec{\tau}_{\sigma\sigma'} d_{m\sigma'}, \quad L_m = i \sum_{m'm''} \sum_\sigma \epsilon_{mm'm''} d_{m'\sigma}^\dagger d_{m''\sigma},$$



In particular, this hamiltonian implements
Hund's rules
(1925 – Z.Physik
'*On atomic spectra of transition metals*')

N electrons in a $M=2l+1$ -fold degenerate shell

- Maximize S [$= N/2$ $N < M$; $= M-N/2$ $N > M$]
- Given S , maximize L
- Given (S,L) lowest $J=|L-S|$ if $N < M$ (less than $\frac{1}{2}$ filling) , highest $J=L+S$ if $N > M$

“The bus-seat rule”

For example a d-shell with 3 electrons (less than half-filling corresponding to 5 electrons) will have $\uparrow, \uparrow, \uparrow, 0, 0$ and with 7 electrons $\uparrow\downarrow, \uparrow\downarrow, \uparrow, \uparrow, \uparrow$. These rules are sometimes referred to as the ‘bus-seat’ rule: singly-occupied spots are filled first, then double occupancies are created when singly-occupied spots are no longer available.



Physical origin: exchange (QM)

- Minimize cost of inter-electron Coulomb repulsion
- Ex: For 2 electrons, $S=1$ forces an antisymmetric orbital wave-function ('electrons further apart'), in contrast to $S=0$
- Actually, screening of nucleus-electron interaction (smaller in singly occupied orbitals) actually plays a key role (cf. Levine, Quantum Chemistry) in lowering the energy of singly-occupied states
- 3rd rule due to spin-orbit

So, what is U_{eff} ? N electrons in M orbitals ($0 \leq N \leq 2M$)

- 1) If $M < N$ (or $M > N$) non half-filled shell: only the interaction between parallel spins matters $U' - J = U - 3J$

$$U_{\text{eff}} = (U' - J) \left[\frac{(N+1)N}{2} + \frac{(N-1)(N-2)}{2} - 2 \frac{N(N-1)}{2} \right] = U - 3J$$

$U_{\text{eff}} = U' = U - 3J$

The Hund's coupling reduces U_{eff}

- 2) If $N = M$ (half-filled shell)

$$| \uparrow\downarrow, \uparrow, \uparrow \rangle \quad E_0(N+1) = (U' - J) \frac{N(N-1)}{2} + U + U'(N-1)$$

$$\begin{aligned} U_{\text{eff}} &= (U' - J) \left[\frac{N(N-1)}{2} + \frac{(N-1)(N-2)}{2} - 2 \frac{N(N-1)}{2} \right] + U + U'(N-1) \\ &= U + (N-1)J \end{aligned}$$

$U_{\text{eff}} = U + (N-1)J$

The Hund's coupling increases U_{eff}

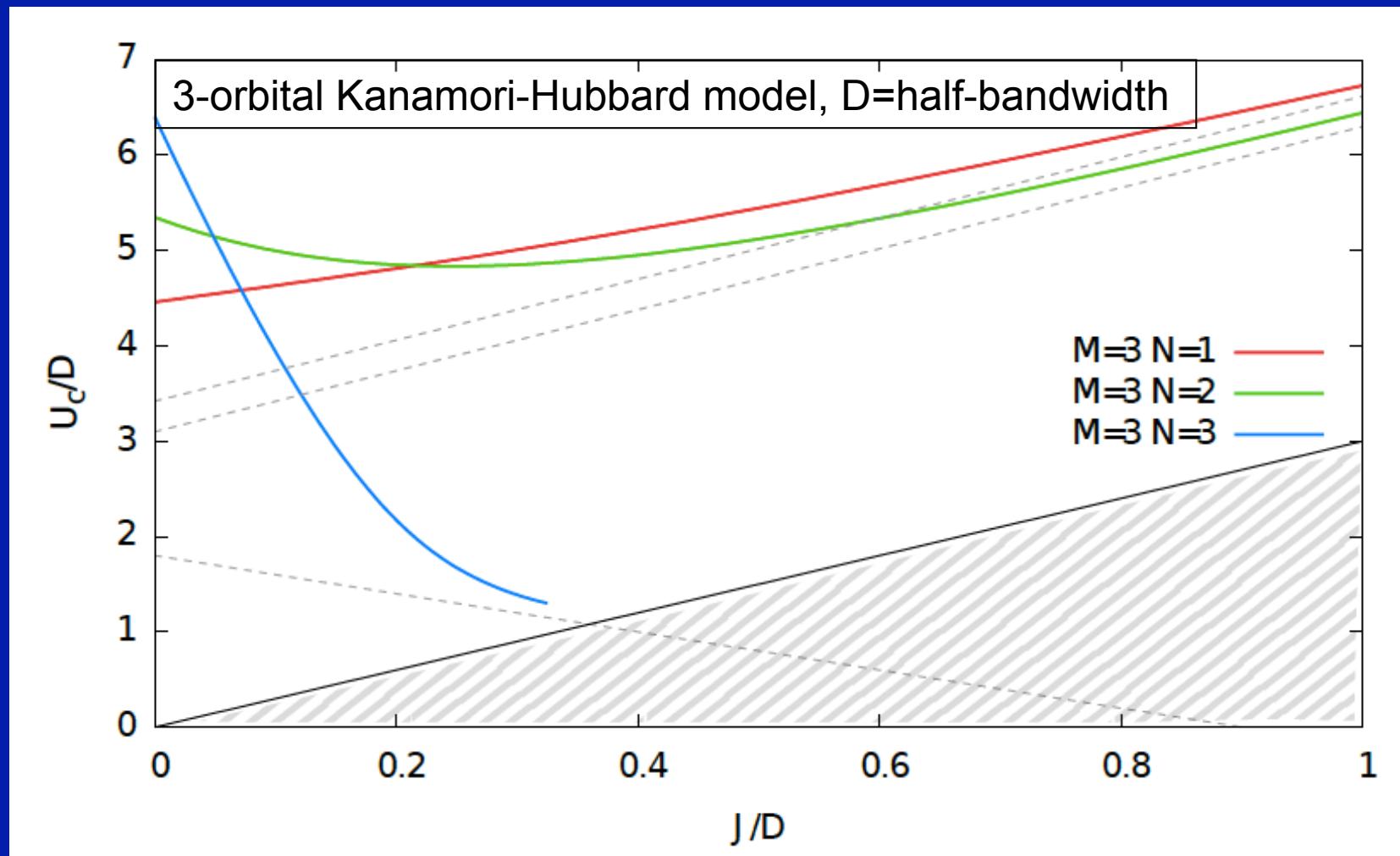
→ Half-filled (sub)shells are usually robust Mott insulators

The critical coupling for
the Mott MIT
depends crucially on
Hund's rule coupling
and on the filling of the shell

cf. van der Marel & Sawatzky PRB 37 (1988) 10674
van der Marel PhD's thesis
L. de' Medici PRB 83 (2011) 205112

Review article:
AG, de'Medici and Mravlje
Annual Reviews Cond. Mat. Phys Vol 4 (2013)
arXiv:1207.3033

More refined calculations using DMFT (t_{2g} shell)



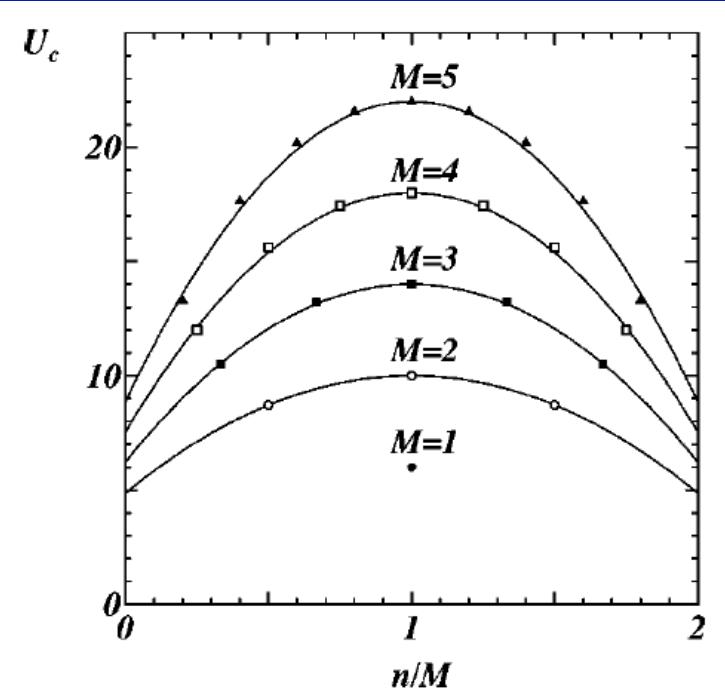
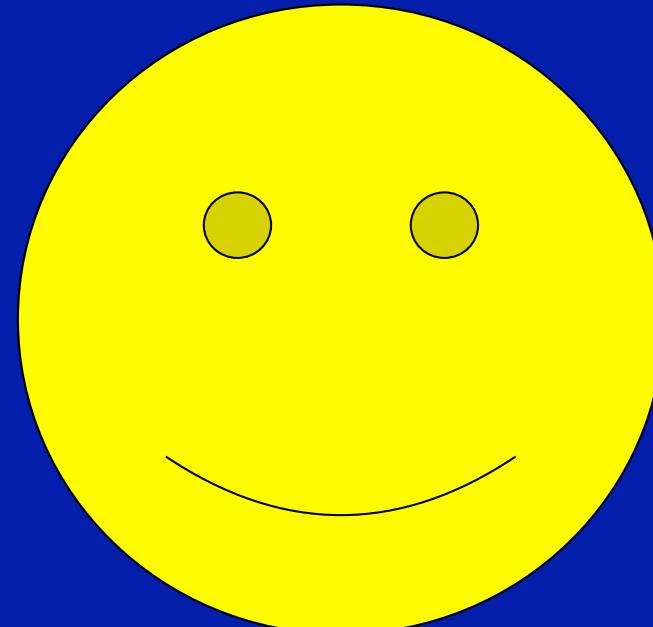
AG, de'Medici and Mravlje
Annual Reviews Cond. Mat. Phys Vol 4 (2013)
arXiv:1207.3033

cf. early work on V_5S_8
Fujimori et al. PRB (1991)

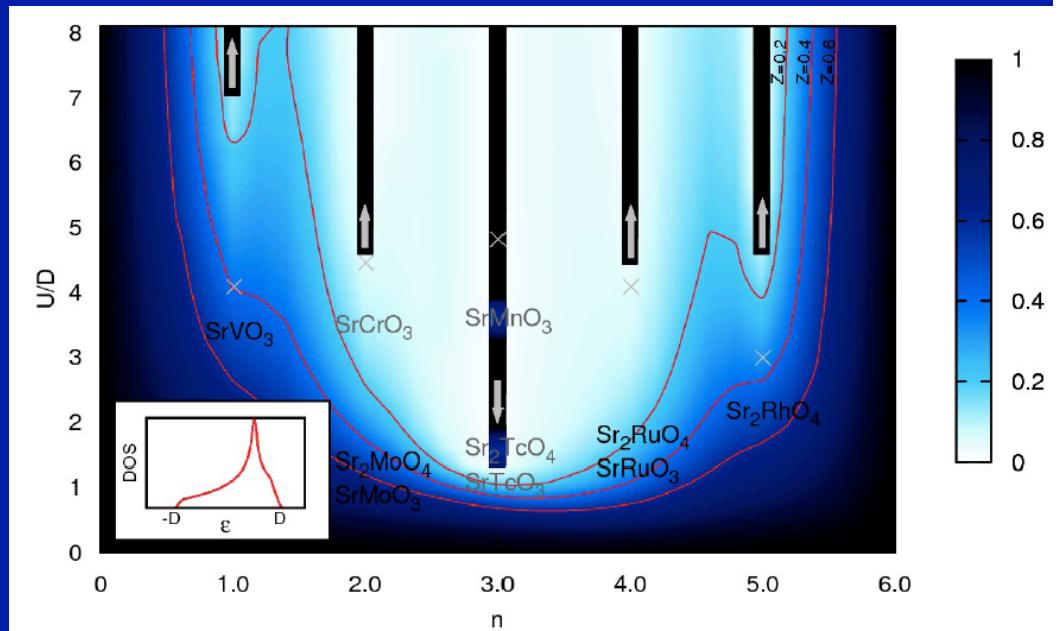
$J=0$



$J \neq 0$



Crucial dependence of U_c on filling

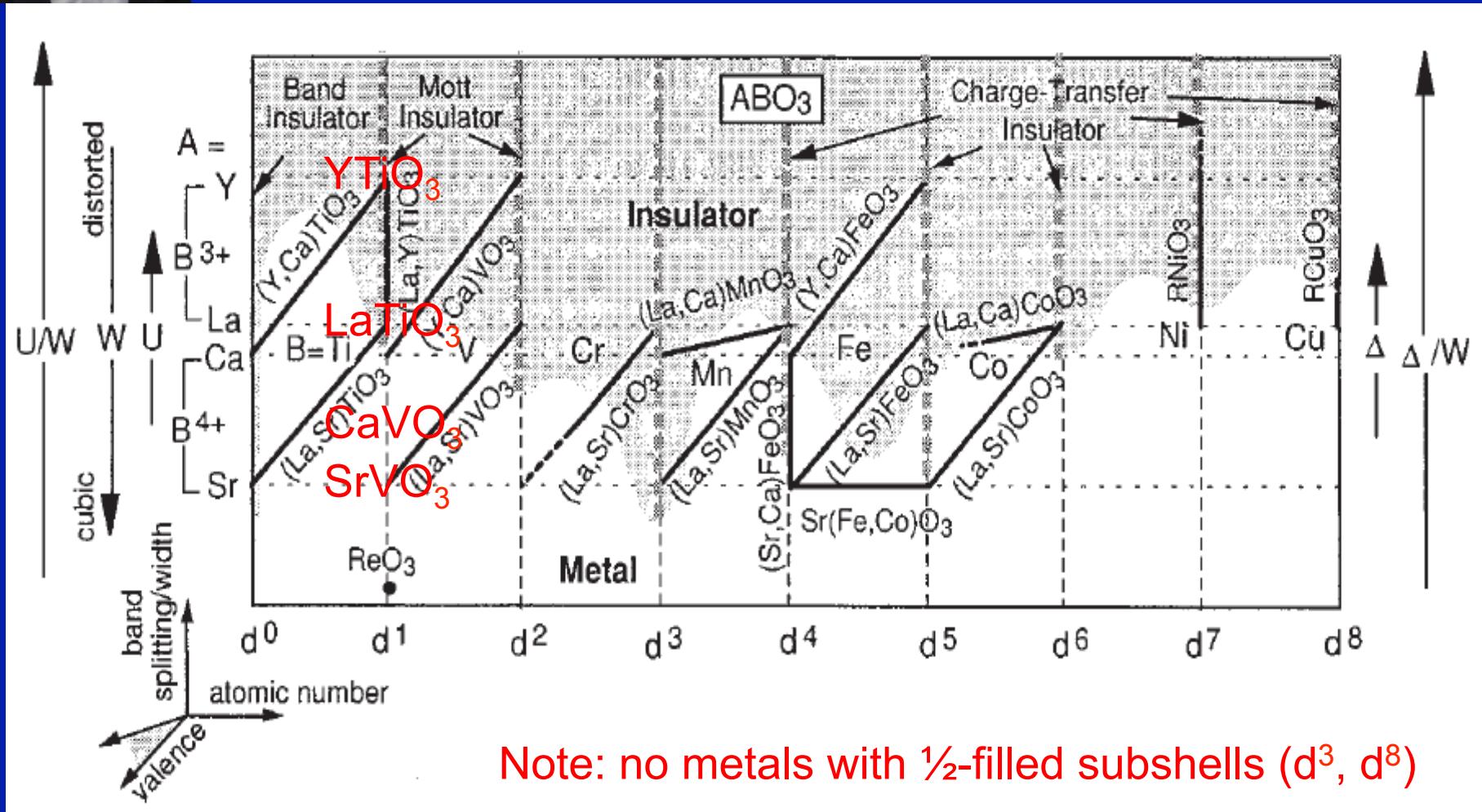




``Atsushi Fujimori's map of RMO_3 perovskites''

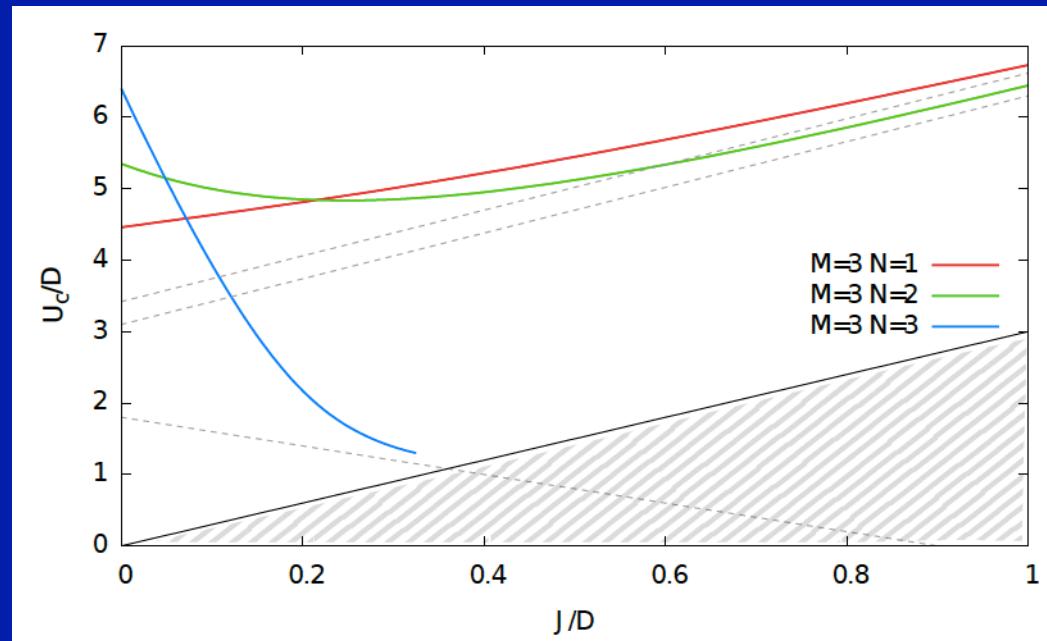
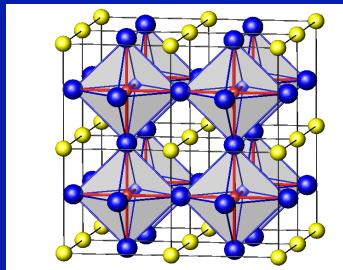
J.Phys Chem Sol. 53 (1992) 1595

Imada, fujimori, Tokura, Rev.Mod.Phys (1998)



Hund's J is crucial to make contact with real-life !

Metallic vanadates vs. Insulating Titanates: solving the puzzle

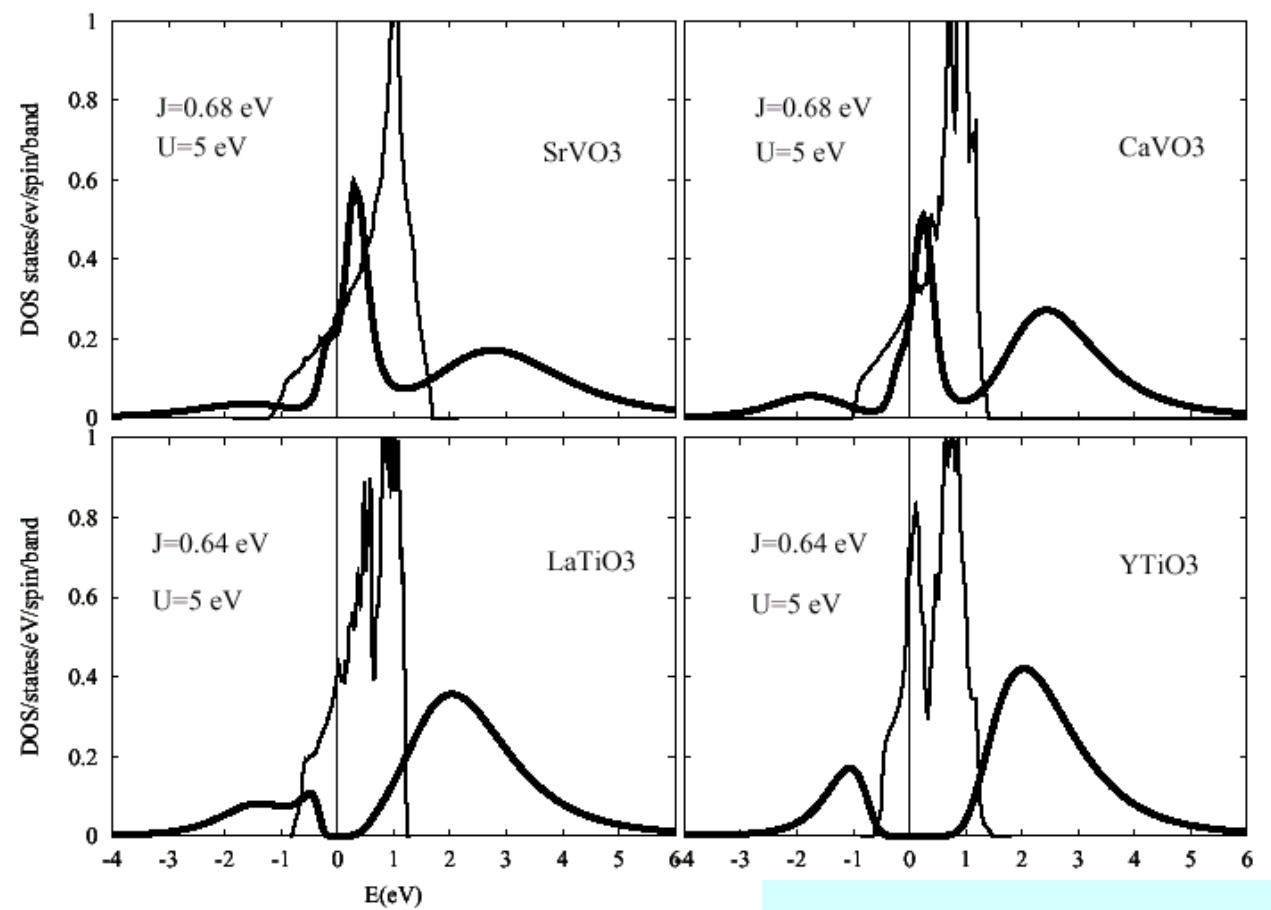
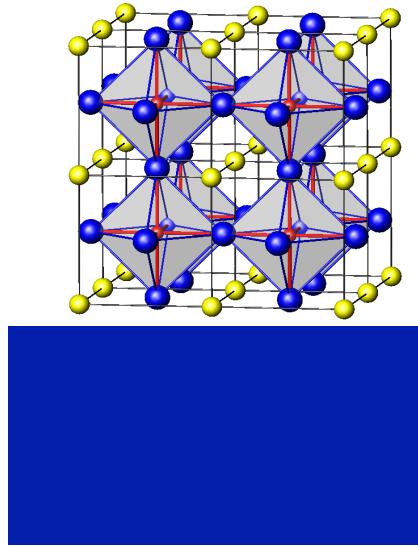


Cubic deg M=3 : $D \simeq 1.5\text{eV}$ $J/D \simeq 0.45 \Rightarrow U_c \simeq 8\text{eV}!$

Full t_{2g} splitting M=1: $D \simeq 1\text{eV} \Rightarrow U_c \simeq 3D = 3\text{eV}!$

Reduction of orbital deg. and Hund's play a key role,
not only/primarily reduction of bandwidth by distortion !

Electronic structure + Many-Body (DMFT) calculations: accounting for metallic/insulating nature of vanadates/titanates

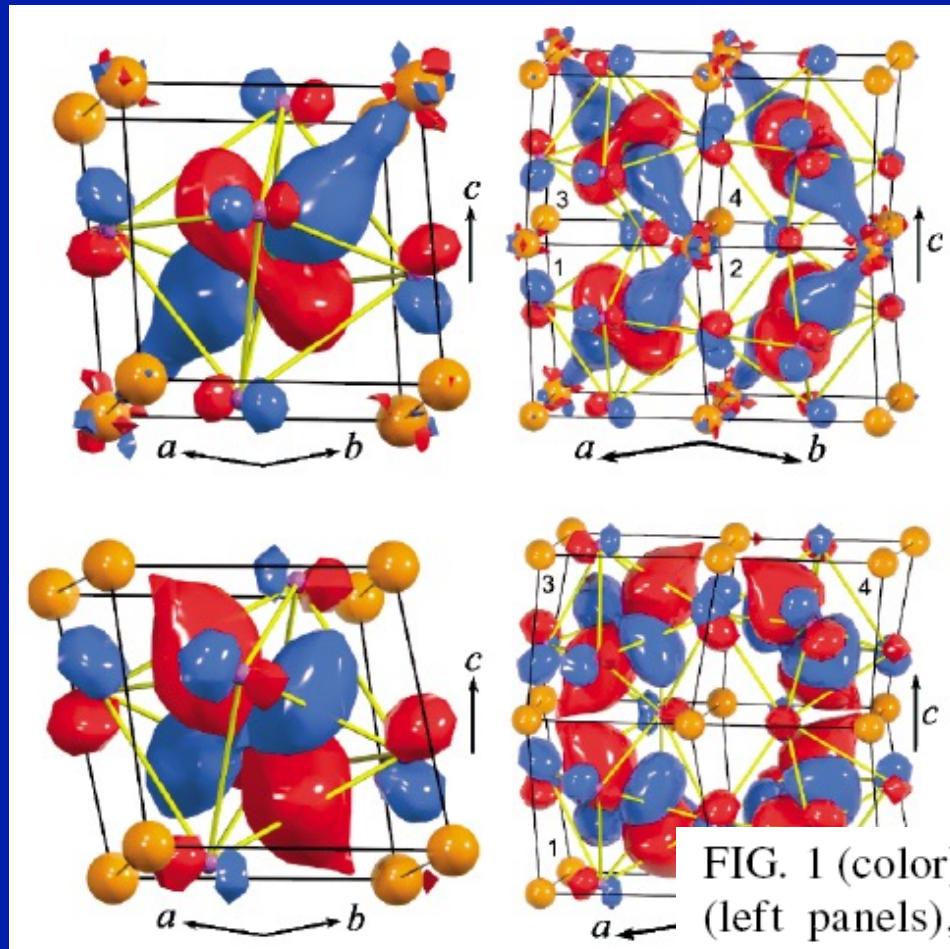


E.Pavarini et al., PRL 2004

cf. also Sekiyama et al. (Ca/SrVO₃)
PRL 2004

- Narrowing of quasiparticle bands due to correlations (the Brinkman-Rice phenomenon)
- Hubbard satellites (i.e extension to the solid of atomic-like transitions)

Correlation-enhanced splitting of t_{2g} shell → Strong orbital polarization predicted in the insulating materials :



LDA+DMFT calculations

$0.586|xy\rangle + 0.275|xz\rangle + 0.762|yz\rangle$ for LaTiO_3
(88% of d^1 electron population)

$0.622|xy\rangle - 0.029|xz\rangle + 0.782|yz\rangle$ for YTiO_3
(96% of d^1 electron population)

FIG. 1 (color). $Pbnm$ primitive cells (right panels), subcells 1 (left panels), and the occupied t_{2g} orbitals for LaTiO_3 (top panels) and YTiO_3 (bottom panels) according to the LDA + DMFT calculation. The oxygens are violet, the octahedra yellow, and the cations orange. In the global, cubic xyz system

Quantitative agreement of DFT+DMFT with experiments Quasiparticles + lower Hubbard band clearly resolved in bulk-sensitive photoemission experiments

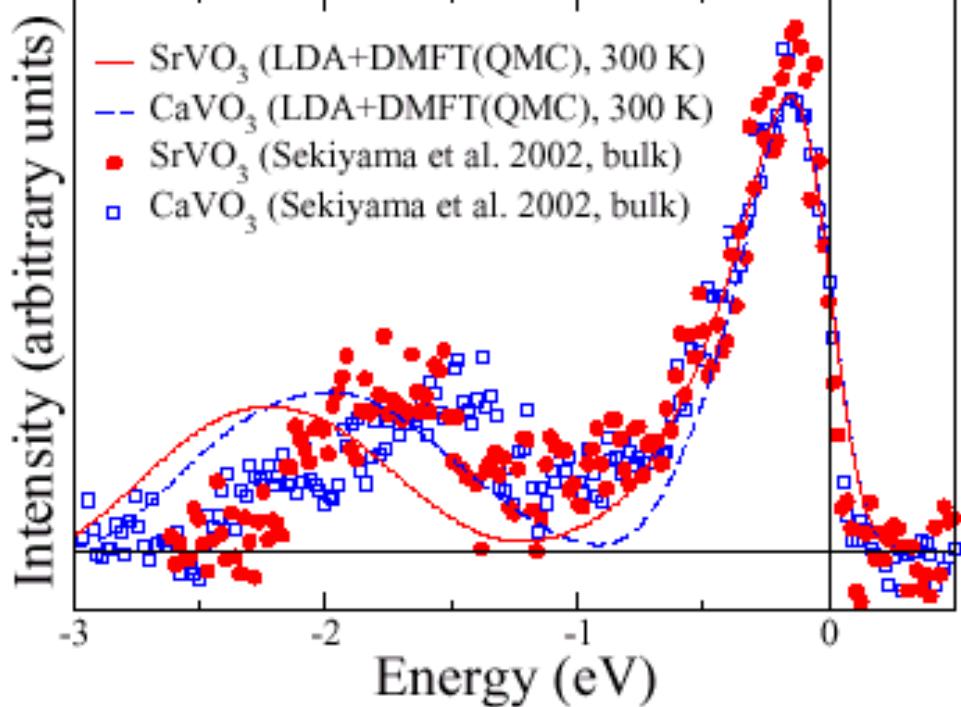


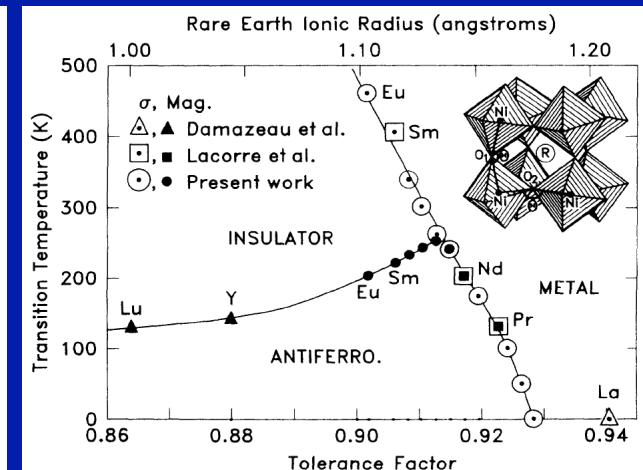
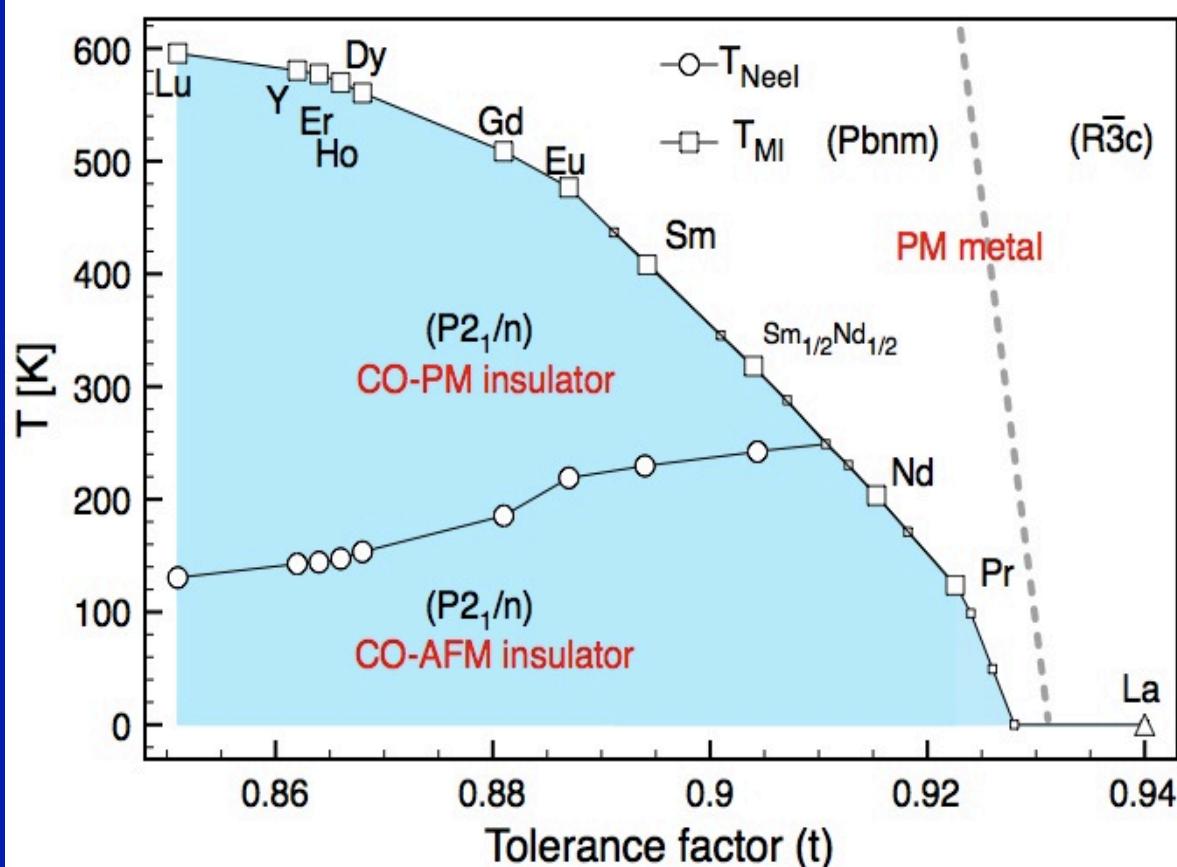
FIG. 4: Comparison of the calculated, parameter-free LDA+DMFT(QMC) spectra of SrVO₃ (solid line) and CaVO₃ (dashed line) with bulk-sensitive high-resolution PES (SrVO₃: circles; CaVO₃: rectangles) [4]. Horizontal line: experimental subtraction of the background intensity.

Sekiyama et al,
Ca/SrVO₃

Lecture III / Part 2

Introduction to Rare-Earth
Nickelates $RNiO_3$
and to their Metal-Insulator
Transition

MIT in Nickelates $RNiO_3$



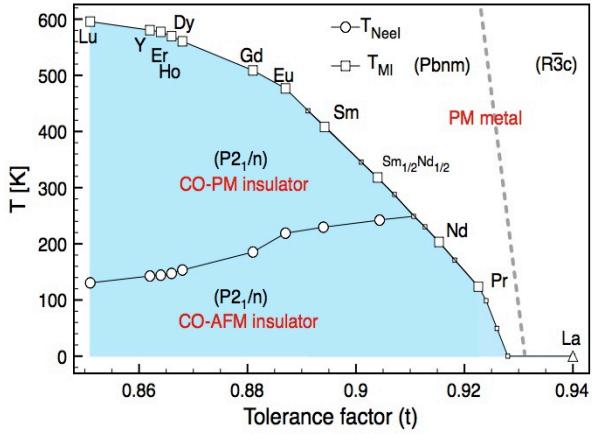
$$t = \frac{d_{R-O}}{\sqrt{2} d_{Ni-O}}$$

Tolerance factor:
smaller t
= Larger distortion



R.Sherwitzl, PhD thesis, Geneva 2012 Adapted from Catalan, *Phase Transitions*, (2008)

Early work: Demazeau et al. (Bordeaux, Hagenmuller's group 1971) Lacorre, Torrance et al. 1992 (IBM San Jose & Le Mans)



MIT of Nickelates: Puzzles

- Naive valence counting (ionic picture):
- $\text{Ni}^{3+} \rightarrow 3d^7 = t_{2g}^6 e_g^1$
- Orbital degeneracy (1 electron in e_g doublet) should lead to strong Jahn-Teller distortion → NOT observed !
- MIT comes with structural bond-disproportionation
- 1st order MIT
- MIT as Mott transition of $\frac{1}{4}$ -filled e_g band NOT a tenable picture (fine-tuning required, structural transition and evolution over the RE series not accounted for, etc... - more below)

Acknowledgements:

THEORY:

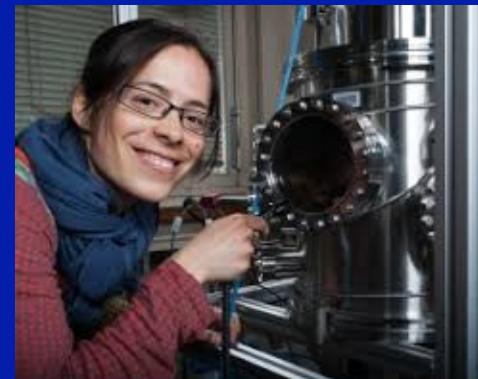
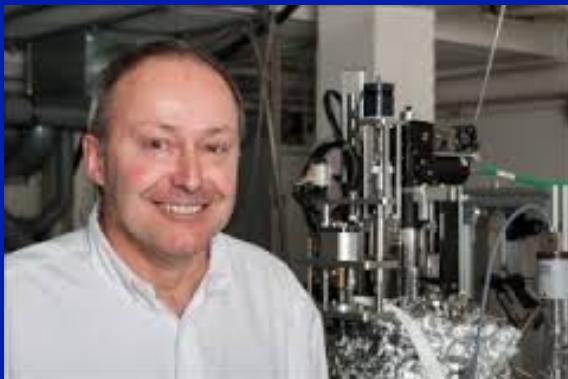
Alaska Subedi
Paris



Oleg Peil
Geneva/Paris
now in Leoben, Austria



EXPERIMENTS:



Dirk van der Marel, Jean-Marc Triscone
University of Geneva

Marta Gibert, Sara Catalano

Why are Nickelates interesting ?
Why renewal of interest
in recent years ?

Controllability / Tunability !

Thin films and heterostructures open new avenues
for these materials.

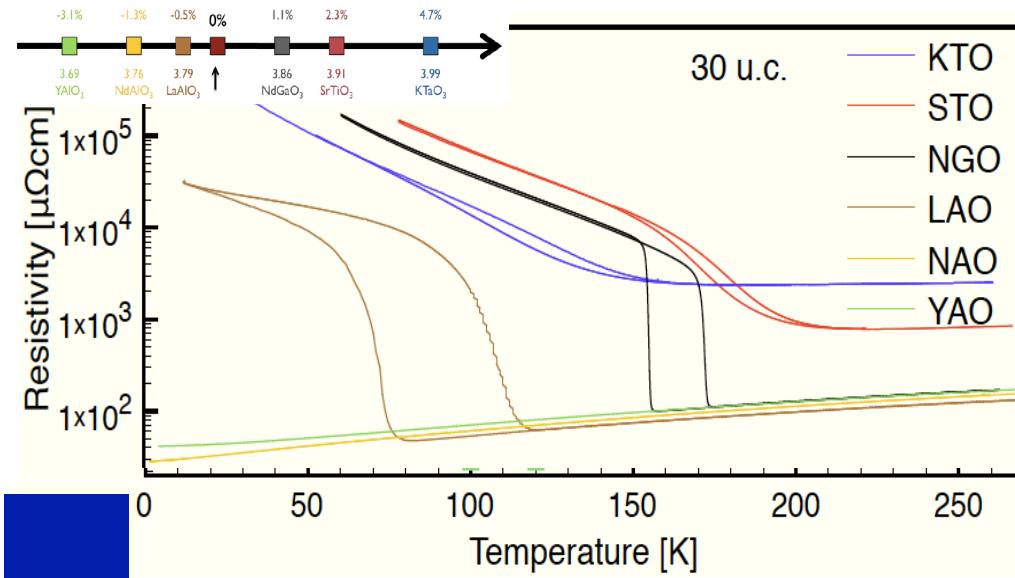
Have been proposed as a way to engineer a
synthetic superconductor through control of orbital
degeneracy
(cf. Lecture 4)

CONTROL: Traditional and Novel routes

Bandwidth	Pressure Size of rare-earth Distortion Tolerance factor 3d,4d,5d metal	Strained thin films and heterostructures Control by Light pulses /'non-linear phononics'
Crystal field, Orbital degeneracy	Size of rare-earth Distortion Tolerance factor	- Same -
Filling of shell, Electron density Doping	Chemistry	Ionic liquids Gating
	$\text{Sr,Ca}^{2+} \rightarrow \text{La, R}^{3+}$	
Interaction strength	3d,4d,5d metal	Tunable dielectric gating ? Light ?
Charge-Transfer	Change apical oxygen distance Change ligand: $\text{O} \rightarrow \text{S, Se...}$	Light ?

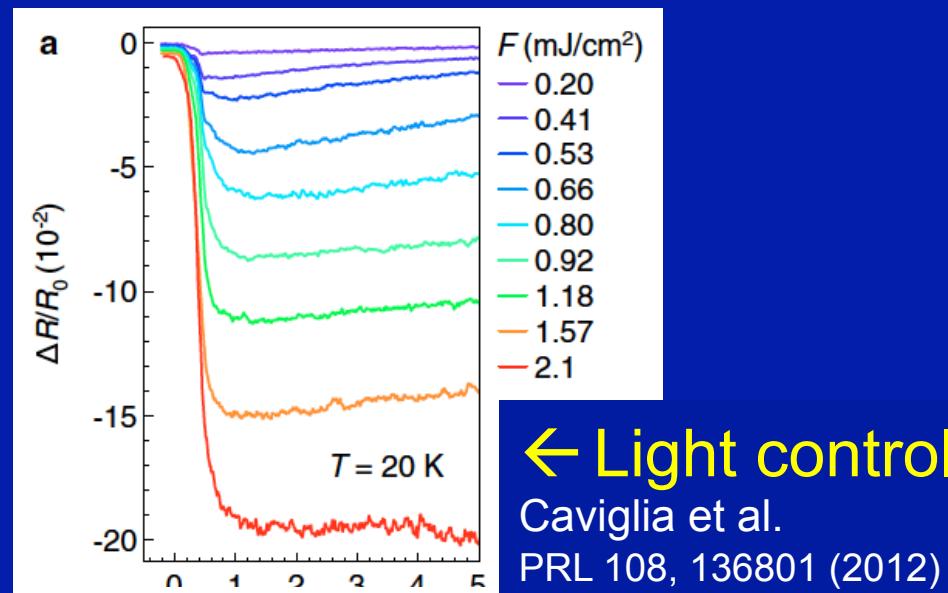
Controllability by: Strain, Gating, Light... Nickelates have it all !

- Beautiful work by several groups over recent years, e.g:
 - Triscone et al. - Geneva
 - Keimer et al. – Stuttgart
 - Cavalleri - Caviglia et al. – Hamburg
 - Ahn et al. – Yale
 - Stemmer et al. – Santa Barbara
 - Chakhalian et al. - Arkansas
 - Hwang et al. – Stanford
 - Bibes, Barthelemy et al. - Palaiseau
 - and several others...

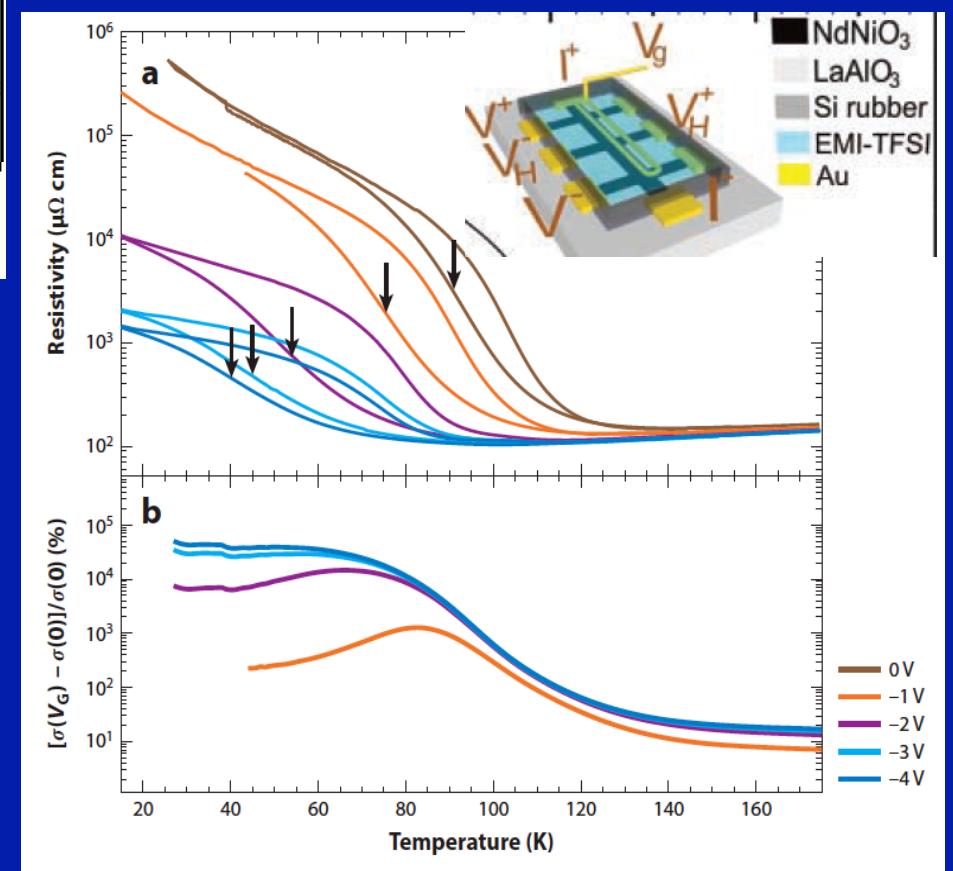
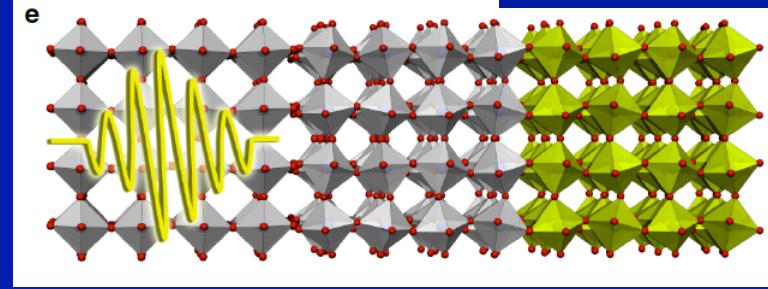


NdNiO₃ ← Strain control

Scherwitzl et al.
PRL 106, 246403 (2012)



← Light control
Caviglia et al.
PRL 108, 136801 (2012)



Ionic liquid gating control

R.Scherwitzl et al.
Adv. Mat. 22, 5517 (2010)